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Hydrogen production from heavy oil in the presence of calcium hydroxide[☆]

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Abstract

A new hydrogen production method, the HyPr-RING process was applied to a vacuum residue of Arabian light crude oil to clarify the effects of added water, calcium hydroxide, which absorbs carbon dioxide, and the reaction temperature. It was determined that when a sufficient amount of calcium hydroxide was present, it provided enough water to produce hydrogen and additional water was not necessary. To consume all of the carbon dioxide in 1 mol of carbon from the feedstock, 25 mol% of calcium hydroxide was needed and hydrogen production was saturated at 50 mol%. Carbon conversion was dependent mainly on the temperature and was slightly dependent on water and pressure. The reaction pressure was as low as 4.2 MPa. Thermal decomposition of the feedstock was the dominant reaction below 600 °C, which produced methane.

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Keywords: Hydrogen production; Water; Calcium hydroxide; Reaction temperature; Selectivity

1. Introduction

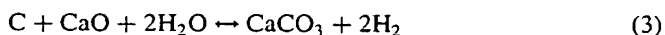
Hydrogen (H₂) is an environmentally clean energy source since pollutants are not generated. In the 21st century H₂ is expected to be a primary energy source for generating electricity, fuel, and other applications. Therefore, an efficient and low-cost H₂ production process will be required to meet the anticipated increase in demand. One of the conventional famous processes for H₂ production is the partial combustion gasification process such as commercially operated TEXACO Processes, which requires two reaction stages [1]. The first is a water–carbon reaction, which is operated above 1000 °C, as shown in Eq. (1) and the second is a water–gas shift reaction as shown in Eq. (2).



However, such a partial combustion process requires CO₂ separation after the CO conversion.

We have proposed a new H₂ production process named the HyPr-RING process [2–5], which uses calcium oxide

(CaO) or/and calcium hydroxide Ca(OH)₂ as the adsorbent of carbon dioxide (CO₂). The merit of this process is that both reactions (Eqs. (3) and (4)) occur in a single stage reactor at a significantly lower temperature (approximately 700 °C) than the water–carbon reaction (greater than 1000 °C) [4,5]. In the HyPr-RING process the Ca(OH)₂ is converted to calcium carbonate (CaCO₃) and simultaneously absorbs the produced CO₂, which results in a dramatic increase in H₂ recovery.



Although the principles of this mechanism are similar to a CO₂ acceptor process [6], the HyPr-RING process has several advantages. One is that the HyPr-RING process generally operates at several MPa of steam pressure. From our previous work, the equilibrium of the CaO–Ca(OH)₂ system [5] (Eq. (5)) lies dominantly towards Ca(OH)₂ when the steam pressure is greater than 1.5 MPa at 700 °C.



This means that Ca(OH)₂ absorbs the CO₂ in a HyPr-RING process, while CaO is the absorbent species in the CO₂ acceptor process. Another advantage is the reaction

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temperature. The higher steam pressure shifts Eqs. (3) and (4) to the right side and more H_2 is produced. Therefore, the HyPr-RING process can be applied at lower reaction temperatures, which may prevent the sintering trouble caused by CaO. Another benefit is that unlike a CO_2 acceptor process, which only uses coal, the HyPr-RING process can produce hydrogen from a variety of sources including coal and organic carbon containing materials such as heavy oil, plastics, and biomasses. Also, hydrogen production is not inhibited by water contained in the feedstock. Among the potential feedstocks, heavy oil is very promising because it is relatively inexpensive, easy to handle as a liquid by heating or using solvents and has low ash content.

In our original proposal [2] the temperature ranged between 600 and 700 °C, but the required pressure was above 25 MPa, which is a supercritical pressure. A large capital investment would be required to create reactors for large-scale commercial plants. Further research [3] revealed that the efficiency of hydrogen production would not be significantly reduced at a subcritical pressure of water and the reaction pressure could be further reduced.

This paper investigated the effects on hydrogen production by varying the amount of additional water, the quantity of $Ca(OH)_2$ used, and the reaction temperature using a heavy oil feedstock. The advantages and disadvantages of a heavy oil feedstock were probed and the feasibility of reducing the reaction pressure was examined.

2. Experimental

2.1. Reactor

The autoclave used in the experiments had an inner volume of 70 cm³ and was equipped with a thermocouple and a pressure transducer (Fig. 1). A vacuum residue of Arabian light oil (C: 84.1 wt%, H: 10.7 wt%, N: 0.2 wt%, S: 4.3 wt%, H/C = 1.52) was used as the feedstock and $Ca(OH)_2$ (Wako Pure Chemical Industries) was used as the CO_2 adsorbent. Approximately 400 mg of feedstock, which contained 28 mmol of carbon, varying amounts of $Ca(OH)_2$ and water, if necessary, were charged into an alumina Tammann tube, which precluded a reaction between the alkaline mixture and the inner reactor wall. To prevent damage to the destruction of a Tammann tube from bumping and other types of collisions, a folded stainless steel mesh was placed between the reactor and the Tammann tube. The effective volume of the reactor with a Tammann tube was reduced to 60 ml. The reaction proceeded in a nitrogen atmosphere. Standard reaction conditions were a temperature of 700 °C and a reaction time of 20 min. The reactor was heated to 700 °C in approximately 45 min using an electric furnace. The reactor was removed from the furnace after the reaction proceeded for

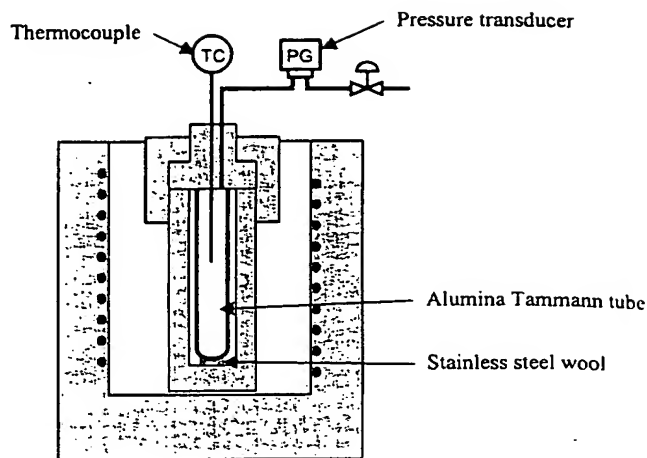


Fig. 1. Schematic diagram of the reactor.

20 min. The reactor was cooled by a fan to 200 °C and was cooled to room temperature with an ice bath.

Runs 1–5 determined the effects of charged water. Run 6 clarified the amount of coke deposited on the inner wall of the reactor, the surface of the Tammann tube, and the mesh. For Run 6, an anti-seizing compound, which is normally applied to bolts at the cap to prevent the reactor from seizing, was not used because the mineral oil in the anti-seizing compound would yield an inaccurate value for the coke deposits, and the reactor was cooled to room temperature using only a fan. The effects of $Ca(OH)_2$ were studied in Runs 7–10, while the effects of the reaction temperature were examined in Runs 11–14. Run 14 was a two stage reaction, which had the following temperature profile:

r.t. (room temperature) → 600 °C (1st stage) → r.t. → 700 °C (2nd stage) → r.t.

The gaseous products from the first stage were extracted at room temperature keeping the reactor closed and then the reactor was heated to 700 °C. The retention times at 600 and 700 °C were both 20 min.

2.2. Gas analysis

When the autoclave reached room temperature, the gas in the reactor was extracted via a needle valve into a sealed flask filled with water. The volume of the gaseous products was measured by the amount of displaced water, which was determined by the difference in the total weight of the flask before and after the gas was introduced. The composition of the gaseous product was analyzed by gas chromatography. The amount of residue was calculated from the weight change of the Tammann tube. The reaction residue raked from the Tammann tube was used to measure the adsorbed carbon dioxide and the residual carbon.

2.3. Recovery

2.3.1. Carbon

All 28 mmol of the carbon charged was from the feedstock. After the reaction, carbon existed as methane, ethane, gaseous CO_2 , calcium carbonate (CaCO_3) and as organic residue. The amount of methane, ethane, and gaseous CO_2 were determined by gas analysis. The amount of CaCO_3 and organic residue were determined as follows:

1. In a two-necked 200 ml flask, 0.5–1 g of the reaction residue and 50 ml of water were magnetically stirred in a water bath. The flask was equipped with a soap-film flow meter with a volume of 100 ml and a dropping funnel.
2. A soap film formed in the lower portion of the flow meter and the position was recorded.
3. A 10 vol% hydrochloric acid aqueous solution was then slowly added, dropwise, to the mixture of the residue and water. The gaseous product pushed up the soap film.
4. After the gas production had ceased, the position of the bubble was recorded, and the volume and the bubble moved, determined the amount of gas produced.
5. The remaining residue in the flask was collected as the organic residue and the carbon content was determined by elemental analysis.

The recovery is expressed as the mol% based on the carbon in the feedstock.

2.3.2. Hydrogen

The amount of hydrogen charged was calculated from the hydrogen content in the feedstock, charged $\text{Ca}(\text{OH})_2$, and water. After the reaction, hydrogen was found in methane, ethane, water, $\text{Ca}(\text{OH})_2$, and organic residue. The amount in methane, ethane, and the organic residue were determined as described in Section 2.3.1. The amount of $\text{Ca}(\text{OH})_2$ in the residue was determined by thermogravimetry, which was conducted up to 900 °C at the heating rate of 10 °C/min in air with a flow rate of 50 ml/min. Often weight loss was observed between 400 and 500 °C and between 500 and 700 °C. The former represents the release of water from $\text{Ca}(\text{OH})_2$, and the latter is the decomposition of CaCO_3 and the combustion of organics. The amount of released water and $\text{Ca}(\text{OH})_2$ were calculated from the former weight loss.

The amount of water was estimated by Eq. (6) because after the reaction water would condense on the inner wall, a lead pipe, and other small spaces of the reactor.

$$R_w = C_w + C_{\text{Ca}(\text{OH})_2} - R_{\text{Ca}(\text{OH})_2} - 2R_{\text{CaCO}_3} - 2R_{\text{CO}_2} \quad (6)$$

Here, R_w , C_w represent the moles of water remaining and charged, respectively. $C_{\text{Ca}(\text{OH})_2}$ and $R_{\text{Ca}(\text{OH})_2}$ indicate the moles of $\text{Ca}(\text{OH})_2$ charged and remaining, respectively, as $\text{Ca}(\text{OH})_2$ is a source of water. R_{CaCO_3} and R_{CO_2} mean the moles of CaCO_3 and CO_2 in gas phase after reaction,

respectively. Using those recoveries, the hydrogen distribution was calculated based on the charged hydrogen.

2.3.3. Oxygen

The amount of charged oxygen was calculated from the oxygen content of the feedstock, charged $\text{Ca}(\text{OH})_2$, and water. After a reaction oxygen existed in gaseous CO_2 , water, $\text{Ca}(\text{OH})_2$, CaCO_3 , CaO , and as organic residue. Using those recoveries, the oxygen distribution was calculated based on the charged oxygen, although the amount in the organic residue was neglected.

3. Results and discussion

3.1. Effects of water

As the reaction pressure was controlled by the amount of water charged in the reactor, the effects of water were evaluated in terms of the amount by adding 0–700 mol% (0–3500 mg, Runs 1–5) of water in the presence of about 96 mol% (2000 mg) of $\text{Ca}(\text{OH})_2$ as shown in Table 1.

The gaseous products of all runs consisted mainly of H_2 and CH_4 with a small amount of C_2H_6 and trace amounts of CO_2 . The reaction pressure increased as more water was added and was ranged from 4.2 (Run 1) to 22.0 MPa (Run 5). The H_2 yields were almost equivalent (38–40 mol%) for Runs 1–4, while the lowest yield, 34 mol%, was obtained when most water was added in Run 5. The yields of CH_4 and CO_2 were similar in Runs 1–5. The results demonstrated that H_2 could be produced with only the water contained in the $\text{Ca}(\text{OH})_2$ molecules. It was also confirmed that the elimination of the additional water leads to a substantial reduction in reaction pressure, 4–5 MPa, which is feasible for commercial scale processes.

Using the ideal gas law, the partial steam pressure in Run 1 estimated from the total pressure and the gas produced was 1.7 MPa. This indicates that more than 50% of $\text{Ca}(\text{OH})_2$ was remained in the reactor at the operating condition [5]. In Runs 2–5, $\text{Ca}(\text{OH})_2$ should be more dominant due to greater partial pressure of water and should be played the role of CO_2 acceptor. It is thought that $\text{Ca}(\text{OH})_2$ was played the role of CO_2 acceptor in Run 1 as well as Run 2–5.

Although the amount of water had a significant effect on the reaction pressure, it did not impact the yields of H_2 and the other gases. The carbon recovery shows that 30–35, 1, and 23–25% of the consumed carbon produced CH_4 , C_2H_6 , and CaCO_3 , respectively. The organic residue contained 12–16% of the carbon. The total carbon recovery was in the range of 66–73%. It is thought that CO_2 including CaCO_3 , resulted from producing H_2 according to Eq. (4).

The balance of H_2 and oxygen are also shown in Table 1. Here, the content of oxygen in the organic residue was neglected because the amount was very small (less than 5 wt%) and it is thought to contain a small amount of ash.

Table 1
Effect of amount of water

	Run 1	Run 2	Run 3	Run 4	Run 5
Charge					
Water (mol%)	0	195	344	349	700
Ca(OH) ₂ (mol%)	96	94	95	96	96
Pressure at reaction temperature (MPa)	4.2	6.2	9.4	8.8	22.0
Partial pressure of water (MPa)	1.7	3.4	6.8	6.1	19.4
Recoveries of products and residues					
H ₂ (mol%)	38	39	38	40	34
CH ₄ (mol%)	30	33	33	33	35
C ₂ H ₆ (mol%)	1	1	1	1	1
CO ₂ (mol%)	0	0	0	0	0
Recovered water ^a (mol%)	32	214	354	377	705
Solid residue					
Ca(OH) ₂ (mol%)	17	26	33	20	46
CaCO ₃ (mol%)	24	25	26	24	22
CaO ^b (mol%)	60	49	40	56	33
Organic residue ^c (wt%)	14	18	17	20	15
Elemental analysis of organic residue (wt%)					
Carbon	87.3	87.0	87.3	88.8	81.8
Hydrogen	2.1	1.9	2.1	2.0	2.0
Nitrogen	0.5	0.5	0.5	0.5	0.5
Sulfur	6.1	6.7	6.1	4.9	3.7
Carbon recovery (% based on charged carbon)					
H ₂	30	33	33	33	35
CH ₄	3	2	2	2	2
C ₂ H ₆	0	0	0	0	0
CaCO ₃	23	24	25	23	21
Organic residue	15	18	17	21	14
Total	69	77	77	79	71
Hydrogen distribution (% based on charged hydrogen)					
H ₂	22	11	7	8	4
CH ₄	35	18	13	13	8
C ₂ H ₆	2	1	1	1	0
Recovered water ^a	20	60	69	73	81
Residual Ca(OH) ₂	9	7	6	4	5
Organic residue	2	1	1	1	0
Total	91	97	97	99	99
Oxygen distribution (% based on charged oxygen)					
CO ₂ (gas)	0	0	0	0	0
Recovered water ^a	18	57	67	70	80
Ca(OH) ₂	17	13	12	7	10
CaCO ₃	35	19	14	13	7
CaO ^b	30	12	7	10	4
Total	100	100	100	100	100

Reaction temperature, 700 °C. Feed, 400 mg (containing 28 mmol of carbon). Based on moles of carbon in feedstock.

^a Calculated by the amounts of charged and recovered Ca(OH)₂ and produced CO₂.

^b Calculated as the balance of Ca salts.

^c wt% based on charged oil.

Although the water recovery is an estimate, more hydrogen and oxygen were recovered than carbon.

3.2. Material balance

In order to determine why the carbon recovery was lower than hydrogen and oxygen, Run 6 was conducted without an anti-seizing compound or water (Table 2). The amount of coke was 23 mol%, and total carbon recovery was as high as 94 mol%. Most of the unrecovered carbon was considered to be in the coke because deposits were observed in every run. The reason why coking occurred could be because the gaseous products had little opportunity to come into contact with Ca(OH)₂ since the reactor in this study had an inner volume of 60 cm³ and a maximum of 2000 mg of Ca(OH)₂ was used. If a reactor was filled with Ca(OH)₂, then coking should not have occurred. Further experiments conducted in a continuous-flow reactor would test this hypothesis.

3.3. Effects of calcium hydroxide

The effects of Ca(OH)₂ on the production of H₂, CH₄, and CO₂ were investigated in the presence of 0–94 mol% of Ca(OH)₂ (Table 3, Runs 2 and 7–10). The amount of water added was between 195 and 199 mol% in order to be in excess of water during reactions. Without Ca(OH)₂ (Run 7), 25 mol% of CH₄ was produced and only 10 mol% of H₂ was produced. The amount of CH₄ gradually increased from 25 to 33 mol% as the amount of Ca(OH)₂ was increased from 0 to 94 mol%. At lower levels of added Ca(OH)₂, H₂ production increased and at approximately 50 mol% of Ca(OH)₂, H₂ production plateaued at approximately 40 mol%.

CO₂ was not observed in the gas phase when the quantity of Ca(OH)₂ was greater than 24 mol%.

Theoretically, 1 mol of carbon reacts with 2 mol of water to produce 1 mol of CO₂ and 2 mol of H₂, and the conversion of CO₂ to CaCO₃ requires 1 mol of Ca as shown in Eqs. (3) and (4). The theory along with the correlation of the quantity of Ca(OH)₂ and the production of H₂ revealed that the amount of carbon consumed to produce H₂ was less than 25 mol%. This means that water including Ca(OH)₂ was enough when 96 mol% of Ca(OH)₂ was added to the feedstock.

3.4. Effects of the reaction temperature

The effects of the reaction temperature were investigated using approximately 96 mol% of Ca(OH)₂ and 0 mol% water with temperatures between 550 and 700 °C (Table 4, Run 1 and Runs 11–13) because previous research has shown that H₂ production is highly dependent on the reaction temperature [3].

CH₄ production linearly increased from 14 to 32 mol% as the reaction temperature was increased. There was a dramatic increase in H₂ production when the reaction

Table 4
Effect of reaction temperature

	Run 11	Run 12	Run 13	Run 1
Reaction temperature (°C)	550	600	650	700
Charge				
96	96	96	96	
Pressure at reaction temperature (MPa)	1.9	1.8	3.1	4.2
Partial pressure of water (MPa)	1.3	1.0	1.6	1.8
Recoveries of products and residues				
H ₂ (mol%)	4	5	21	38
CH ₄ (mol%)	13	18	24	30
C ₂ H ₆ (mol%)	4	5	3	1
CO ₂ (mol%)	0	0	0	0
Recovered water ^a (mol%)	43	41	15	32
Solid residue				
Ca(OH) ₂ (mol%)	43	43	54	16
CaCO ₃ (mol%)	3	3	10	23
CaO ^b (mol%)	51	50	32	57
Organic residue ^c (wt%)	18	17	20	14
Elemental analysis of organic residue (wt%)				
80.4	87.7	84.6	87.3	
Hydrogen	2.6	2.5	2.3	2.1
Nitrogen	0.7	0.7	0.6	0.5
Sulfur	5.3	5.9	7.8	6.1
Carbon recovery (% based on charged carbon)				
H ₂	13	18	24	30
CH ₄	8	11	7	3
C ₂ H ₆	0	0	0	0
CaCO ₃	3	3	10	23
Organic residue	46	42	30	15
Total	70	74	71	69
Hydrogen distribution (% based on charged hydrogen)				
H ₂	2	3	12	22
CH ₄	16	21	28	35
C ₂ H ₆	7	9	6	2
Recovered water ^a	28	27	13	20
Residual Ca(OH) ₂	25	25	32	9
Organic residue	10	8	6	2
Total	88	93	97	91
Oxygen distribution (% based on charged oxygen)				
CO ₂ (gas)	0	0	0	0
Recovered water ^a	25	24	11	18
Ca(OH) ₂	44	44	56	17
CaCO ₃	4	5	15	35
CaO ^b	26	26	17	30
Total	99	99	99	100

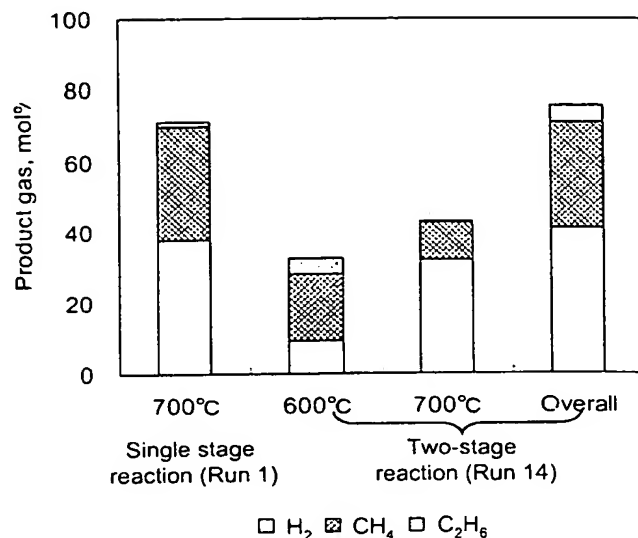
Reaction temperature, 700 °C. Feed, 400 mg (containing 28 mmol of carbon). No water was added. Based on moles of carbon in feedstock.

^a Calculated by the amounts of charged and recovered Ca(OH)₂ and produced CO₂.

^b Calculated as the balance of Ca salts.

^c wt% based on charged oil.

decomposition dominated the process. In all the experiments discussed earlier, the selectivity of H₂ was always less than 50%, which is lower than using coal as the feedstock. A possible reason for the lower selectivity was that the CH₄ produced during thermal decomposition at



The first-stage reaction was carried out at 600°C. After product gas was recovered at room temperature, the second-stage reaction was carried out at 700°C.

Fig. 2. Gaseous product yields from a two-stage reaction.

lower temperatures remained in the gas at higher temperatures and suppressed the selectivity of H₂. To test this hypothesis, a two-stage reaction was conducted (Run 14, Fig. 2).

The reaction at 600 °C produced 32 mol% of gas, which was approximately 60% CH₄. The reaction in the second stage at 700 °C produced an additional 32 mol% of gas, which was 74% H₂. The second stage reaction using the heavy oil produced H₂ with comparable selectivity using coal as the feedstock. The overall gaseous product volume and H₂ selectivity were similar to the single-stage reaction (Run 1). These observations support the hypothesis that the CH₄ produced at lower temperatures, inhibits H₂ selectivity at higher temperatures. These results also suggest that materials with a low H/C ratio such as asphaltene, petroleum pitch, petroleum cokes, or other materials would achieve a higher H₂ selectivity because less CH₄ would be produced through thermal decomposition of the feedstock.

4. Conclusion

From our research the following observations are made regarding the H₂ production from heavy oil in the presence of Ca(OH)₂:

1. The water present in Ca(OH)₂ is sufficient to produce H₂ and additional water is not necessary. H₂ is produced at pressures as low as approximately 4.2 MPa.
2. Carbon conversion is mainly dependent on temperature and is not strongly dependent on water or pressure.

Table 2
Material balance of the reaction without water

	Run 6
Reaction temperature (°C)	700
Charge	
Ca(OH) ₂ (mol%)	96
Pressure at reaction temperature (MPa)	4.4
Partial pressure of water (MPa)	1.9
Recoveries of products and residues	
H ₂ (mol%)	38
CH ₄ (mol%)	32
C ₂ H ₆ (mol%)	1
CO ₂ (mol%)	6
Recovered water ^a (mol%)	7
Solid residue	
Ca(OH) ₂ (mol%)	35
CaCO ₃ (mol%)	22
CaO ^b (mol%)	40
Organic residue ^c (wt%)	10
Coke ^d	23
Elemental analysis of organic residue (wt%)	
Carbon	83.5
Hydrogen	2.1
Nitrogen	0.4
Sulfur	13.3
Carbon recovery (% based on charged carbon)	
H ₂	32
CH ₄	2
C ₂ H ₆	0
CaCO ₃	23
Organic residue	14
Coke ^d	23
Total	94
Hydrogen distribution (% based on charged hydrogen)	
H ₂	22
CH ₄	37
C ₂ H ₆	2
Recovered water ^a	17
Residual Ca(OH) ₂	12
Organic residue	2
Total	92
Oxygen distribution (%) based on charged oxygen	
CO ₂ (gas)	0
Recovered water ^a	15
Ca(OH) ₂	21
CaCO ₃	36
CaO ^b	27
Total	99

Reaction temperature, 700 °C. Feed, 400 mg (containing 28 mmol of carbon). No water was added. Based on moles of carbon in feedstock.

^a Calculated by the amounts of charged and recovered Ca(OH)₂ and produced CO₂.

^b Calculated as the balance of Ca salts.

^c wt% based on charged oil.

^d Carbon deposit on inner wall of reactor, a Tammann tube and a mesh.

temperature was greater than 600 °C, while only 4 mol% was produced below 600 °C. The amount of residual carbon rapidly decreased as the H₂ production increased. On the other hand, the H/C ratio of residue dropped sharply from

Table 3
Effect of amount of calcium hydroxide

	Run 7	Run 8	Run 9	Run 10	Run 2
Charge					
Water (mol%)	196	196	199	197	195
Ca(OH) ₂ (mol%)	0	10	24	48	94
Pressure at reaction temperature (MPa)	5.5	5.0	5.5	5.5	6.2
Partial pressure of water (MPa)	4.2	3.3	3.2	2.9	3.4
Recoveries of products and residues					
H ₂ (mol%)	10	16	31	38	39
CH ₄ (mol%)	25	28	30	30	33
C ₂ H ₆ (mol%)	0	1	1	1	1
CO ₂ (mol%)	2	1	0	0	0
Recovered water ^a (mol%)	193	188	191	187	217
Solid residue					
Ca(OH) ₂ (mol%)	0	0	0	10	24
CaCO ₃ (mol%)	0	7	16	24	24
CaO ^b (mol%)	0	2	8	14	46
Organic residue (wt% ^c)	43	13	17	18	18
Elemental analysis of organic residue (wt%)					
Carbon	87.8	80.0	70.2	87.6	87.0
Hydrogen	1.7	1.6	1.4	2.0	1.9
Nitrogen	0.7	0.5	0.4	0.5	0.5
Sulfur	4.3	2.0	3.0	5.7	6.7
Carbon recovery (% based on charged carbon)					
H ₂	25	28	30	30	33
CH ₄	1	1	2	2	2
C ₂ H ₆	2	1	0	0	0
CaCO ₃	0	7	16	24	24
Organic residue	45	12	14	19	18
Total	72	51	62	76	77
Hydrogen distribution (% based on charged hydrogen)					
H ₂	4	6	10	12	11
CH ₄	18	20	20	19	18
C ₂ H ₆	0	1	1	1	1
Recovered water ^a	0	0	0	3	7
Residual Ca(OH) ₂	71	67	64	58	60
Organic residue	4	1	1	2	1
Total	97	95	96	95	97
Oxygen distribution (% based on charged oxygen)					
CO ₂ (gas)	2	1	0	0	0
Recovered water ^a	98	87	77	64	57
Ca(OH) ₂	0	0	0	7	13
CaCO ₃	0	10	19	25	19
CaO ^b	0	1	3	5	12
Total	100	100	100	100	100

Reaction temperature, 700 °C. Feed, 400 mg (containing 28 mmol of carbon). Based on moles of carbon in feedstock.

^a Calculated by the amounts of charged and recovered Ca(OH)₂ and produced CO₂.

^b Calculated as the balance of Ca salts.

^c wt% based on charged oil.

1.53 in the feedstock to 0.39 even at 500 °C, suggesting the decomposition of the side chains to gaseous hydrocarbons such as CH₄. Overall, it is believed that below 600 °C, H₂ was not produced from water and that the thermal

3. To consume all of the CO₂ present in the feedstock, at least 25 mol% of Ca(OH)₂ is necessary and 50 mol% of Ca(OH)₂ is required to saturate H₂ production.
4. CH₄ is produced mainly by the thermal decomposition of the feedstock and decomposition is the dominant reaction below 600 °C.
5. Using heavy oil as the feedstock, yields a large amount of CH₄ in the gaseous products, which reduces H₂ selectivity.
6. The thermal decomposition of the feedstock presumably forms CH₄.

These results demonstrate that the HyPr-RING process is feasible for commercial use. By controlling the amount of water, a practical pressure can be maintained and the H₂ yield can be maximized by adding a sufficient amount of Ca(OH)₂, which has been theoretically determined based on

the amount of CO₂. The H₂ selectivity can be improved by using a feedstock with a lower H/C ratio.

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